



Vibrational energy levels and predissociation lifetimes of the $A^2\Sigma^+$ State of SH/SD radicals by photodissociation spectroscopy

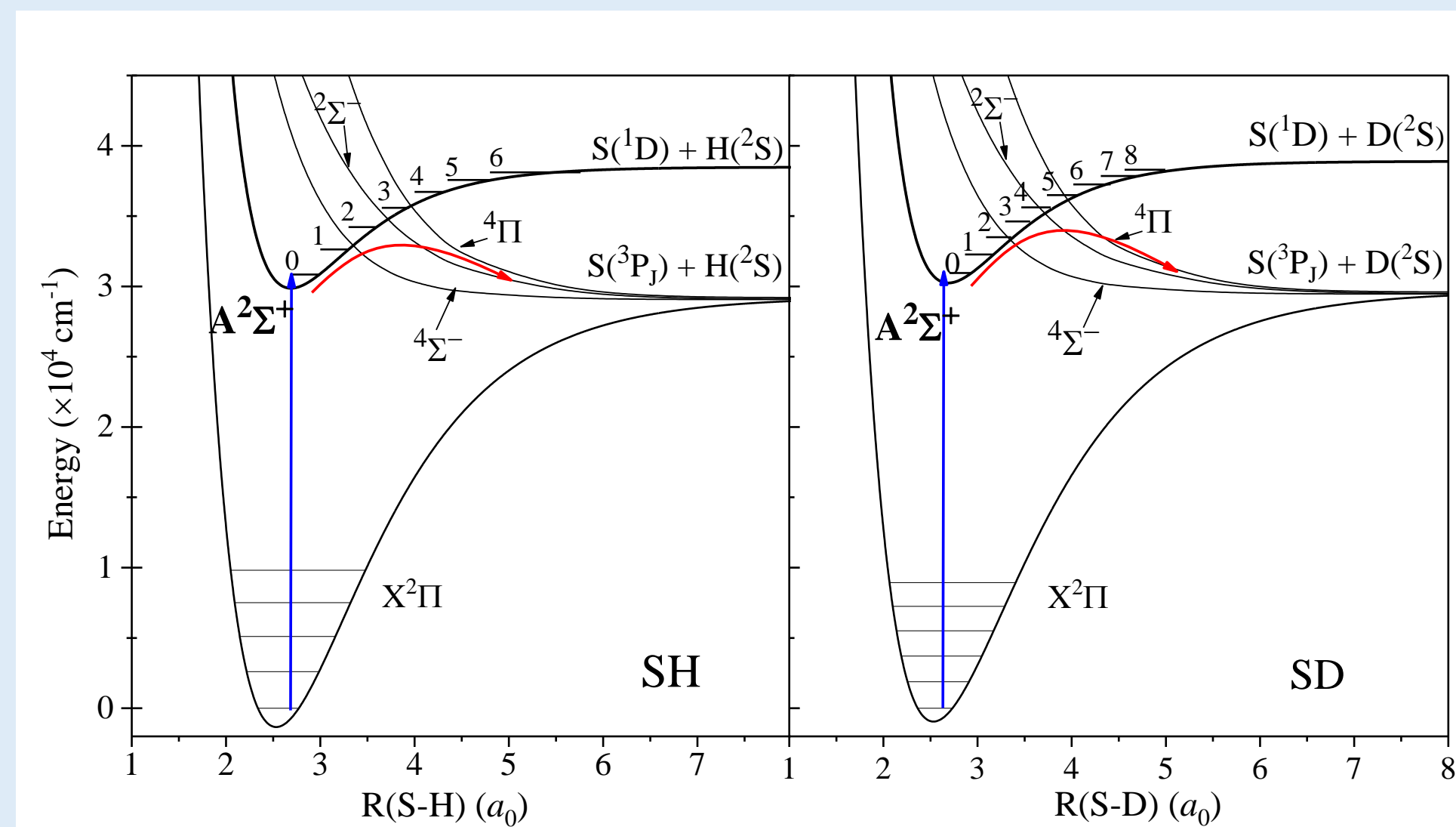
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Introduction

Mercapto radical (SH):

- The SH radical plays an important role in atmospheric sulfur cycle, fossil fuel combustion, and interstellar medium.
- The $A^2\Sigma^+$ state undergoes predissociation via the spin-orbit couplings with three repulsive states ($^4\Sigma$, $^2\Sigma$, and $^4\Pi$), leading to the $H(^2S) + S(^3P_J)$ products.
- Photo-predissociation of the SH $A^2\Sigma^+$ state competes with fluorescence, thus hinders the experimental characterization.

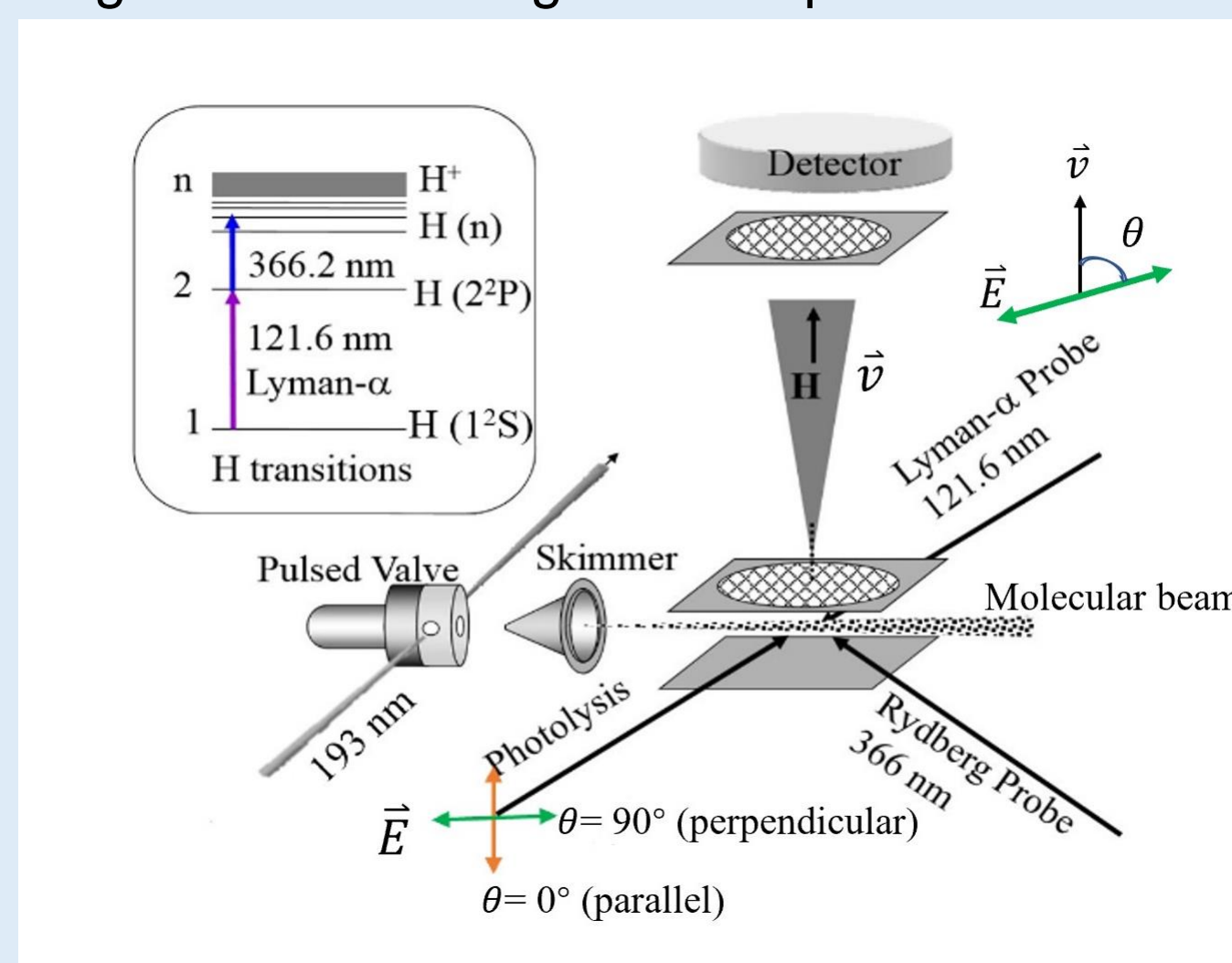
All vibrational levels of the $A^2\Sigma^+$ state ($v = 0-6$ for SH and $v = 0-8$ for SD) are probed by the high- n Rydberg atom time-of-flight (HRTOF) technique. By measuring the H/D + $S(^3P_J)$ product translational energy distributions from photodissociation of SH and SD via the A-X transition, the photofragment yield (PFY) spectra from specific rovibrational levels of the $A^2\Sigma^+$ state are obtained. From the PFY spectra the predissociation lifetimes and the vibrational origins of the A state are determined.



H. Sun and coworkers, *Chem. Phys. Lett.* **194**, 485 (1992)
M. Manna, *Int. J. Quantum Chem., Quantum Chem. Symp.* **29**, 577 (1995)
F. Ornellas and coworkers, *J. Chem. Phys.* **115**, 2178 (2001)

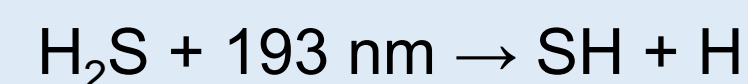
Method and Experimental Setup

High- n Rydberg atom time-of-flight technique

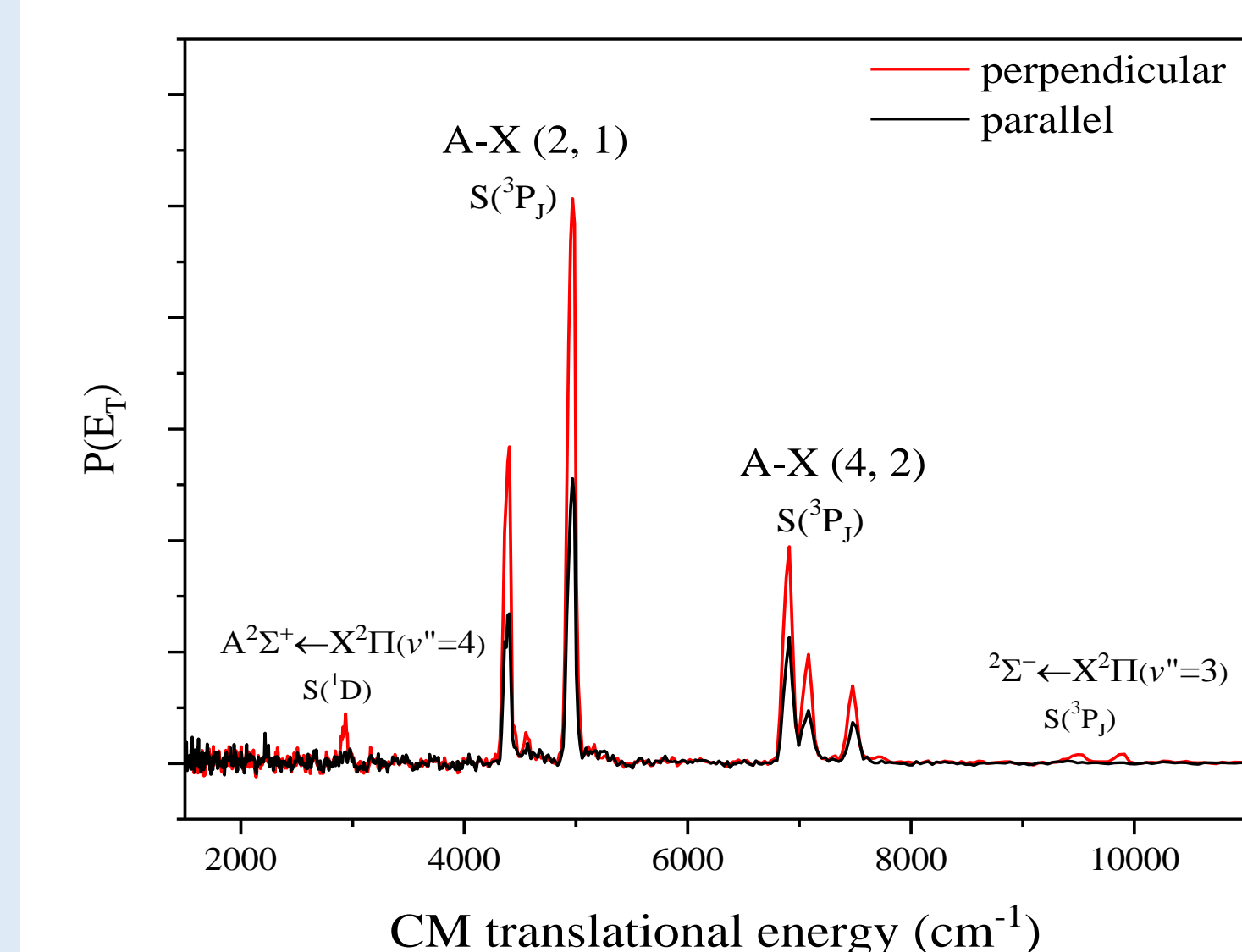


K. Welge and coworkers, *J. Chem. Phys.* **92**, 7027 (1990)

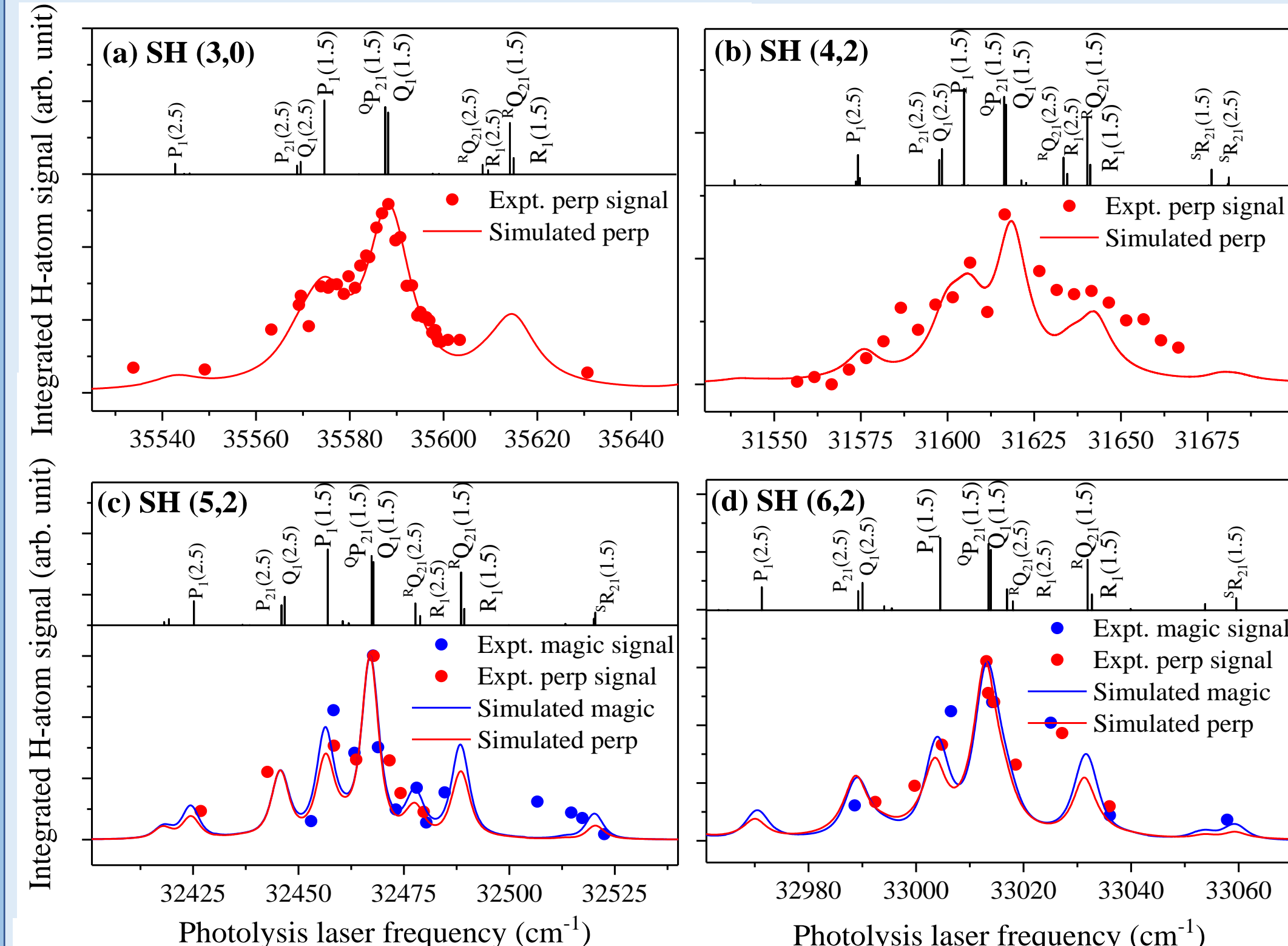
SH radical production:



Results



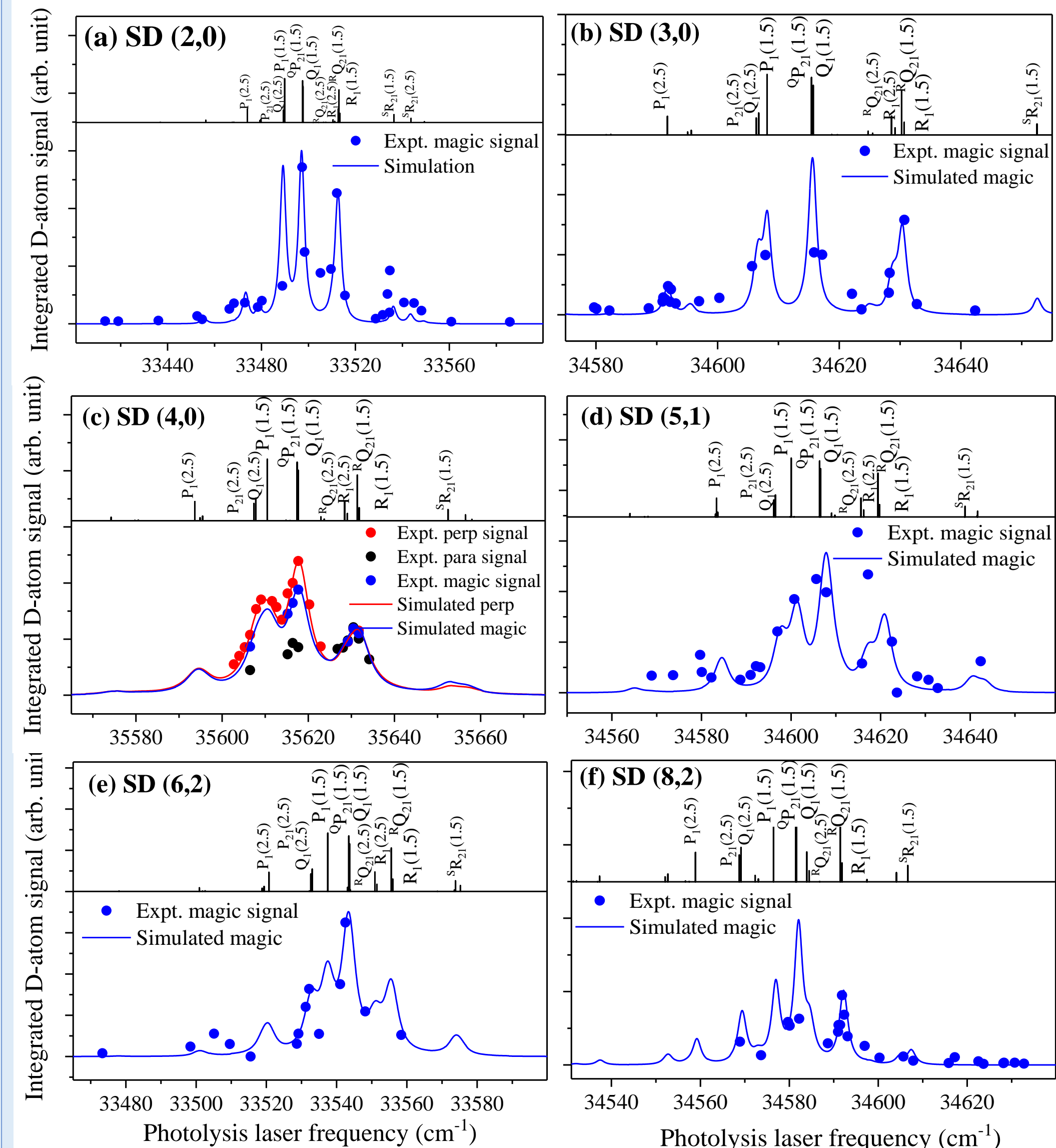
Center-of-mass H + S product translational energy distribution, $P(E_T, \theta)$'s, from photodissociation of SH at 31622.14 cm $^{-1}$, which is the resonance position of the $A^2\Sigma^+ \leftarrow X^2\Pi(2,1)$ $Q_1(1,5)$, $Q_{P21}(1,5)$ transition. The $P(E_T)$ distributions are converted from the TOF spectra, and the products from different pathways are labeled.



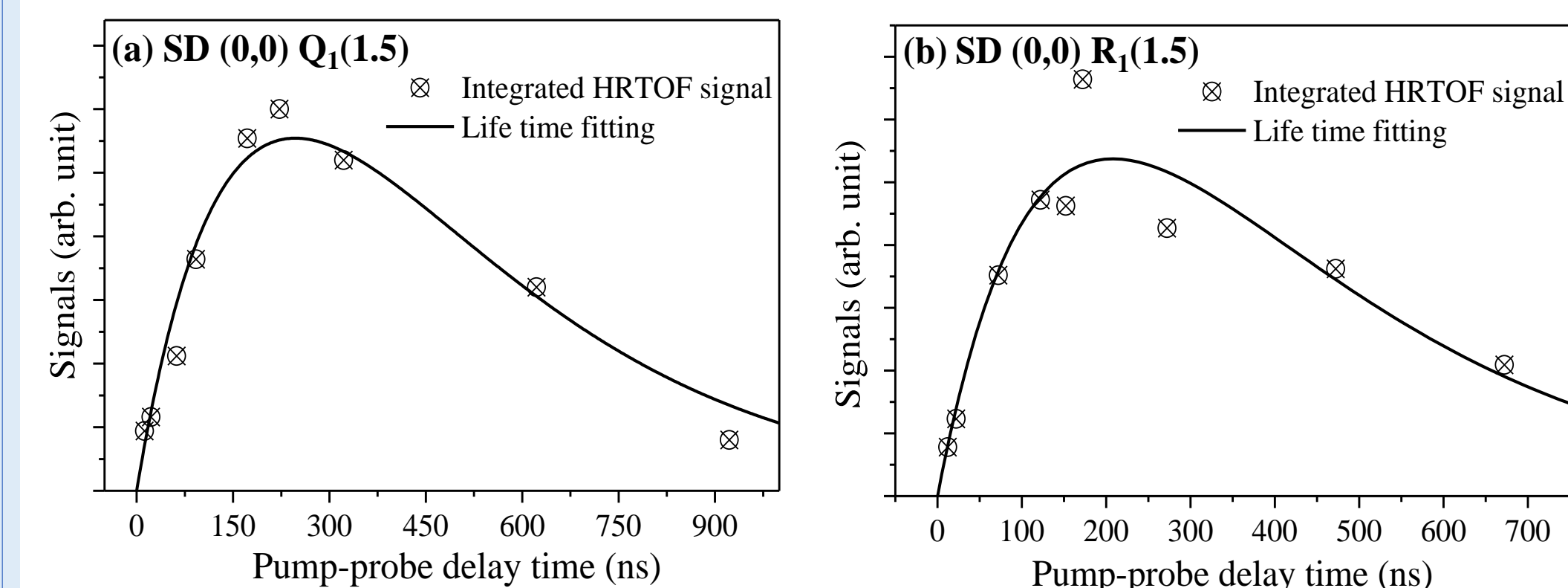
PFY spectra and simulations of the SH $A^2\Sigma^+ \leftarrow X^2\Pi$ absorption bands (a) (3,0), (b) (4,2), (c) (5,2), and (d) (6,2). The experimental signals are the integration of the $H(^2S) + S(^3P_J)$ peaks from predissociation of SH ($A^2\Sigma^+$, $v = 3-6$) in the $P(E_T, \theta)$'s. The intensity at perpendicular polarization is obtained by weighing the simulated total absorption spectrum (equivalent to PFY at magic angle) from *PGOPHER* with an angular factor of $(1 - \frac{1}{2} \times \beta)$, where the anisotropy parameter β is simulated by the program *Betaofnu*. In the simulations, $T = 30$ K in (a), and $T = 45$ K in (b)-(d); the Gaussian FWHM (laser linewidth) = 0.3 cm $^{-1}$, the Lorentzian FWHM (natural linewidth) is (a) 10.0 cm $^{-1}$, (b) 11.0 cm $^{-1}$, (c) 4.8 cm $^{-1}$, and (d) 4.4 cm $^{-1}$.

PGOPHER program, C. M. Western, *J. Quant. Spectrosc. Radiat. Transf.* **186**, 221 (2017)

Betaofnu program, P. Houston and coworkers, *J. Chem. Phys.* **125**, 13, 133316 (2006)



PFY spectra and simulations of the SD $A^2\Sigma^+ \leftarrow X^2\Pi$ absorption bands (a) (2,0), (b) (3,0), (c) (4,0), (d) (5,1), (e) (6,2), and (f) (8,2). In the simulations, $T = 25$ K, the Gaussian FWHM (laser linewidth) = 0.3 cm $^{-1}$, the Lorentzian FWHM (natural linewidth) is fitted to be (a) 3.0 cm $^{-1}$, (b) 1.5 cm $^{-1}$, (c) 5.9 cm $^{-1}$, (d) 3.6 cm $^{-1}$, (e) 4.5 cm $^{-1}$, and (f) 2.2 cm $^{-1}$.



D-atom product temporal profile from predissociation of SD via $A^2\Sigma^+$, $v = 0$, (a) $N = 1$, and (b) $N = 2$. The signals were obtained by integrating the $D(^2S) + S(^3P_2)$ product peaks from the HRTOF spectra of SD via (a) the $Q_1(1,5)$ and (b) $R_1(1,5)$ transition at various photolysis pump probe delay times. The solid line is the fitting result of the D-atom product time profile:

$$S_D(t) = N[\exp(-k_2 t) - \exp(-k_D t)]$$

I. Oref and coworkers, *J. Chem. Phys.* **93**, 5700 (1990)

v'	Predissociative lifetimes			Vibrational levels (cm $^{-1}$)		
	This work	Expt	Calc ^[3]	This work	Expt ^[4]	Calc ^[3]
0		3.37±0.13 ns ^[1]	6.3 ns	0	0	0.0
1		5.45 ps ^[2]	10.6 ps	1784.42±0.4	1784.5±1.0	1783.56
2			2.3 ps	3374.01±0.3	3373.7±1.0	3368.88
3	0.53±0.05 ps		0.95 ps	4742.19±0.8	4742.8±5.0	4745.23
4	0.48±0.14 ps		0.24 ps	5871.88±2	5880.1±10.0	5913.23
5	1.1±0.4 ps		5.9 ps	6724.10±0.7		6847.40
6	~1.0 ps		0.95 ps	7270.91±1.2		7513.93

[1] A. Fast and S. A. Meek, 2021.

[2] M. D. Wheeler, et al., 1997.

[3] S.Y. Lee and H.S. Seon, 2001.

[4] L. Schnieder, et al., 1990.

v'	N'	Predissociative lifetimes			Vibrational levels (cm $^{-1}$)		
		This work	Expt ^[1]	Calc ^[2]	This work	Expt ^[3]	Calc ^[4]
0	0		247±10 ns	43.65 ns	0	0	0
1		339±100 ns					
2		218±100 ns	230±5 ns				
3							
1	0		35 ps	46.63 ps	1319.18±0.1	1319.30±0.05	1319.28
2	0-3	1.8±0.3 ps	2.31 ps	2.27 ps	2540.23±0.3	2540.9±0.2	2540.54
3	0-3	3.5±0.9 ps		7.02 ps	3659.85±0.3		3659.85
4	0-3	0.9±0.2 ps		0.91 ps	4662.23±0.4		4672.33
5	0-3	1.5±0.3 ps		0.47 ps	5536.88±2		5572.38
6	0-3	1.2±0.2 ps		1.69 ps	6306.33±0.3		6353.56
7				1.03 ps	~6889.38		
8	0-3	2.4±0.4 ps		2.33 ps	7345.95±0.8		

This work: assume $\tau_{rad}(SD, v=0) = 910$ ns.

[1] M. D. Wheeler, et al., 1997.

[2] at $N = 0$ level, V. Brites, et al., 2008.

[3] J. Johns and D.A. Ramsay, 1961.

[4] M. N. Gorman, et al., 2019.

Summary

The $A^2\Sigma^+ \leftarrow X^2\Pi(v, v')$ bands for SH $v = 0-6$ and SD $v = 0-8$ are characterized by photodissociation spectroscopy in this study using the high- n Rydberg atom time-of-flight (HRTOF) technique.

The predissociation times for SH $v = 3-6$, as well as SD $v = 0$ ($N = 1$ and 2) and $v = 2-6$ and 8 are determined from the H/D atom PFY spectra and pump probe delay profiles. The lifetime measurements indicate predissociation rates for the $A^2\Sigma^+$ state depend markedly on the vibrational level, in agreement with the previous theoretical studies.

This work also provides the vibrational state energy for the $A^2\Sigma^+$ state, in which the lower energy levels $v = 0-4$ for SH and $v = 0-2$ for SD agree well with previous studies, and the higher levels $v = 5-6$ for SH and $v = 3-8$ for SD are determined for the first time. The derived vibrational origins of the $A^2\Sigma^+$ state suggest further theoretical investigation at high vibrational levels is needed.

Acknowledgement

